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VANADIUM-GALLIUM SYSTEM
BETWEEN 50 AND 100
ATOMIC PERCENT VANADIUM**

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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SUMMARY

✓ PHASE DIAGRAMS ✓
The vanadium-gallium (V-Ga) system within the compositional range from 50 to 100 atomic percent V was investigated. Samples prepared by melting were studied by X-ray diffraction and metallographic techniques after slow cooling from 1100° C. The superconducting V_3Ga phase was found to exist over a very limited compositional range. At room temperature, V_3Ga exists in equilibrium with either V_6Ga_5 (for compositions containing less than 75 atomic percent V) or a Ga saturated V solid solution (for compositions containing more than 75 atomic percent V). Both V_6Ga_5 and the V solid solution are nonsuperconducting at 4.2° K. The microstructures of samples near 75 atomic percent V (V_3Ga) were essentially identical whether compositions were slightly hypostoichiometric or slightly hyperstoichiometric. ✓

INTRODUCTION

The vanadium-gallium (V-Ga) system is of particular interest because it contains the superconducting compound V_3Ga . In reference 1, the critical field H_c at 0° K for this compound is estimated to be in excess of 500 kilogauss. Although superconductivity properties of V_3Ga have been presented in the literature, little metallurgical information is available. In addition to V_3Ga , the compounds V_5Ga_3 , VGa , V_6Ga_5 , and V_2Ga_5 have been reported (see refs. 2 to 5).

V_3Ga has a cubic beta-tungsten type structure, and several authors (refs. 1, 6, and 7) have alluded to the fact that this compound exists as a solid solution over a wide compositional range (66 to 80 atomic percent V). On the other hand, reference 8 reports a constant lattice parameter for V_3Ga within the composition range of 75 to 83 atomic percent V and the presence of a second phase in the microstructure of such samples.

These observations are indicative of limited solubility. Reference 5 also reports limited solubility of approximately 0.5 atomic percent at 800° C. Thus, there would appear to be some question as to the true compositional limits of the V₃Ga phase.

V₅Ga₃ is reported to be stable only in the temperature range from 935° to 1195° C (ref. 5); however, no structural information is available. Reference 5 discusses a VGa phase with a superlattice α -Fe structure, while reference 4 reports a V₆Ga₅ phase as hexagonal. Because of the proximity of the compositions of these phases and the possibility of ambiguous X-ray data, it is not possible at this time to clearly state that these are two distinct compounds. The V₂Ga₅ compound is reported (ref. 4) to have a tetragonal crystal structure (isostructural with Mn₂Hg₅) and to melt peritectically at 1085° C.

The objectives of this investigation were to obtain information regarding the solubility range of V₃Ga, to determine the phases in equilibrium with V₃Ga, to describe the microstructures, and to ascertain the presence or absence of superconductivity in these phases. To this end, compositions within the range from 50 atomic percent V to 100 atomic percent V were prepared by melting under an argon atmosphere. In an attempt to obtain equilibrium structures, all samples were annealed at 1100° C for 1½ hours and slow cooled. Chemical analysis, X-ray diffraction patterns, and microstructures were obtained for each sample. Selected samples were tested for superconductivity at 4.2° K.

APPARATUS AND PROCEDURE

The vanadium and gallium used in this investigation were in chunk form with purities of 99.83 weight percent V and 99.99 weight percent Ga, respectively. All compositions were melted in yttria-stabilized zirconia boats. No evidence of a reaction between the zirconia boats and the charge was found. Melting was accomplished in a tungsten resistance furnace that was first evacuated to a pressure of 10⁻⁵ millimeter of mercury and then backfilled with high-purity argon to a pressure of 500 millimeters of mercury.

The charge was heated to a temperature where liquefaction appeared complete (1600 to 1800° C depending on composition) as judged by visual examination through an optical pyrometer. The specimens were held at the liquefaction temperature for 1/2 hour and then cooled at a rate of approximately 20° C per minute. The samples were then annealed under an argon atmosphere at 1100° C for 1½ hours followed by a slow cool (20° C/min).

Chemical analyses (both V and Ga) and X-ray diffraction patterns were taken of all samples after annealing. Table I lists the compositions studied and the phases present. Samples will be identified in this report by their V content after annealing.

Diffraction patterns at room and elevated temperatures were taken after grinding the samples to -325 mesh powder. Nickel-filtered copper K α radiation was used with a scanning speed of 1/8° per minute. In the case of the high-temperature X-ray

TABLE I. - SAMPLE COMPOSITIONS

As-mixed composition, atomic percent		Resulting composition after melting followed by 1100° C 1½- hour anneal, atomic percent		Phases present
Vanadium	Gallium	Vanadium	Gallium	
51	49	52.7	47.2	V ₆ Ga ₅ + V ₃ Ga
70	30	69.4	30.6	V ₆ Ga ₅ + V ₃ Ga
73	27	74.5	25.3	V ₃ Ga + V ₆ Ga ₅
75	25	74.8	25.1	V ₃ Ga + V ₆ Ga ₅
74	26	76.2	23.4	V ₃ Ga + V-Ga solution
80	20	77.0	20.8	V-Ga solution + V ₃ Ga
85	15	85.6	14.3	V-Ga solution

runs, a helium atmosphere was employed. Lattice constants were obtained from the X-ray diffraction patterns using a least-square analysis programed for the 7090 computer.

The superconductivity results were obtained from electrical resistivity measurements (voltage drop technique with sensitivity of 10^{-8} volt) at 4.2° K. Microhardness measurements were made using a diamond indenter with a 100-gram load. The values are reported as diamond pyramid hardness (DPH) numbers.

RESULTS AND DISCUSSION

The results of this investigation are presented in terms of increasing V content with each subsection being identified by the major phase or phases present.

V₆Ga₅

The compound V₆Ga₅ (theoretical composition, 54.54 atomic percent V) has been previously reported by two investigators (refs. 3 and 4). In reference 4, its composition is given as 54±2 atomic percent V; V₆Ga₅ is reported to be hexagonal with lattice parameters of $a_0 = 8.496 \pm 0.001$ angstroms and $c_0 = 5.174 \pm 0.001$ angstroms. Whether this is the same compound reported in reference 5 as VGa is not clear at this time. The X-ray results of the present investigation are in agreement with those of reference 4; therefore, the compound in the vicinity of 50 atomic percent V will be referred to as V₆Ga₅ in this report.

In this investigation, a specimen containing 52.7 atomic percent V was prepared in

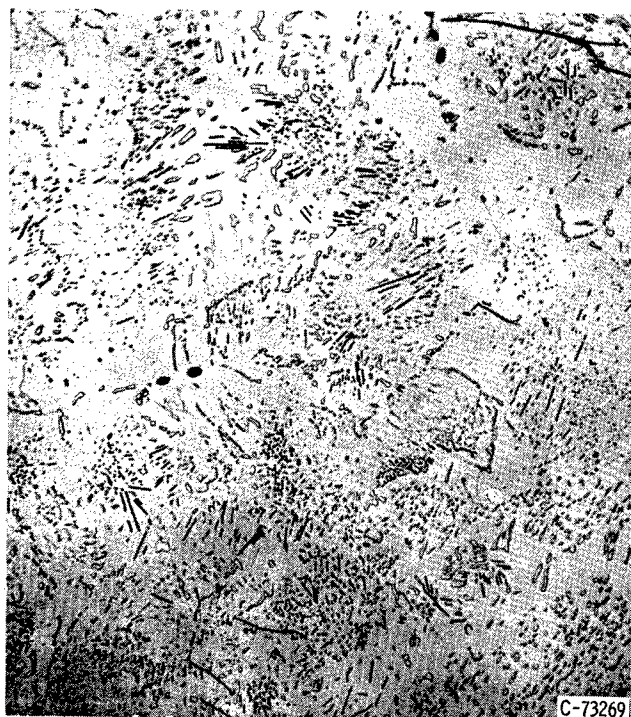
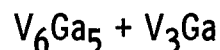


Figure 1. - Microstructure of sample containing 52.7 atomic percent vanadium. Primary phase, V_6Ga_5 matrix; secondary phase, V_3Ga . Etchant, $4H_2O-3HNO_3-1HF$; X250.

the manner described. All but one of the lines present in the X-ray diffraction pattern could be ascribed to V_6Ga_5 using the lattice constants of reference 4. The one remaining line of relative intensity of ≈ 2 percent was believed to be the $\{210\}$ reflection of V_3Ga . Photomicrographs of this sample also showed a second phase present, presumably V_3Ga (fig. 1). The chemical analysis indicates this sample is within the limits reported for V_6Ga_5 in reference 4. The suggested presence of V_3Ga , however, indicates that the actual composition of the V_6Ga_5 compound is less than 52.7 atomic percent V. Microhardness measurements of the V_6Ga_5 phase gave a value of 1000 DPH.



For V contents between 52.7 and 75 atomic percent, the only phases present were V_6Ga_5 and V_3Ga . All lines of X-ray patterns could be identified as either V_6Ga_5 or V_3Ga , with the V_3Ga lines increasing in intensity as the V content increased.

A typical microstructure within this composition range is shown in figure 2 for a sample containing 69.4 atomic percent V. An X-ray pattern obtained from this sample at $1127^\circ C$ showed only V_6Ga_5 and V_3Ga phases present, while at $1327^\circ C$ only V_3Ga lines were detected. Upon cooling to room temperature, the V_6Ga_5 lines reappeared. These results failed to show the presence of any high-temperature phase such as V_5Ga_3 reported by reference 5. Thus, it would appear that the microstructure of figure 2 is the result of either a eutectic or peritectic reaction occurring between 1127° and $1327^\circ C$. The microhardness measurements seem to indicate that the white phase of figure 2 is V_3Ga . This phase resulted in a hardness of 920 DPH, which was identical to that measured for V_3Ga (discussed in the following section).



As mentioned in the INTRODUCTION, there are conflicting views in the literature regarding the solubility limits of the V_3Ga phase. Attempts to obtain single-phase V_3Ga

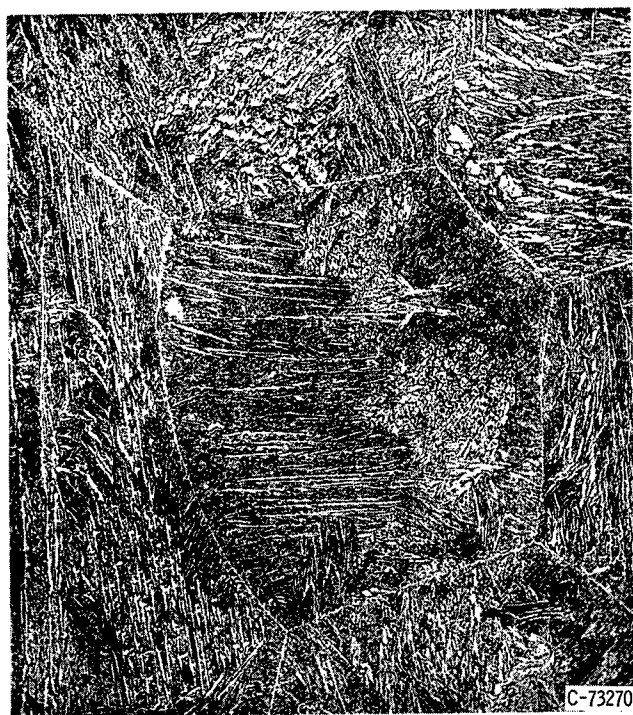


Figure 2. - Microstructure of sample containing 69.4 atomic percent vanadium. V_3Ga (white) + V_6Ga_5 . Etchant, $4H_2O-3HNO_3-1HF$; X100.

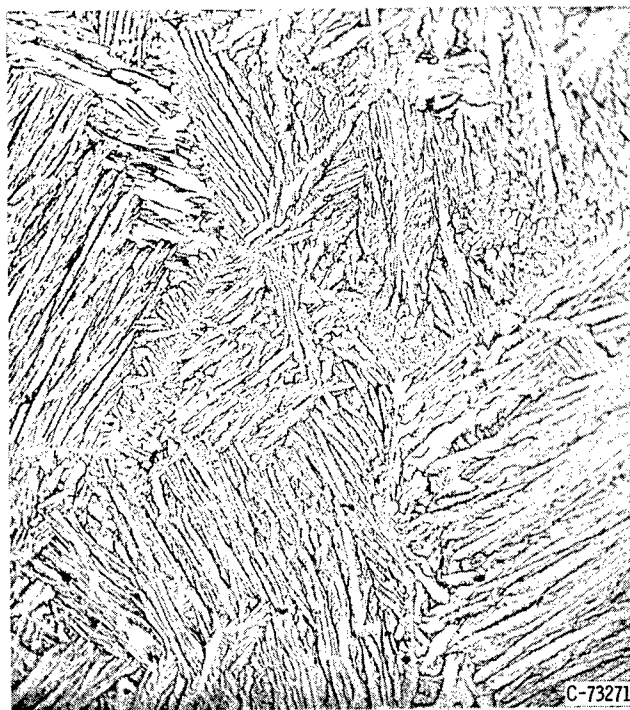


Figure 3. - Microstructure of sample containing 74.8 atomic percent vanadium. Primary phase, V_3Ga (white); secondary phase, V_6Ga_5 . Etchant, $4H_2O-3HNO_3-1HF$; X250.

samples in this study were unsuccessful. Samples containing 74.5, 74.8, 76.2, and 77.0 atomic percent V were examined, and none of these were single-phase materials. Typical microstructures of samples near stoichiometric composition are shown in figures 3 and 4. A comparison of figures 3 and 4 reveals that essentially the same microstructure results regardless of whether the composition is slightly hypostoichiometric (atomic percent $V < 75$, fig. 3) (or hyperstoichiometric (atomic percent $V > 75$, fig. 4). Definite evidence of a second phase is offered in figure 5. This electron photograph of the 74.8 atomic percent V sample magnified 14 000 times definitely shows the particles of a second phase.

Quenching near-stoichiometric samples from the annealing temperature of $1100^{\circ}C$ resulted in essentially the same microstructure, although a somewhat finer distribution resulted. Reference 5 also shows a second phase present in near-stoichiometric compositions. However, the distribution of the second phase differs from that shown in figures 3 and 4. This difference may be due to the long annealing times (800 hr) used in reference 5.

X-ray diffraction of these near-stoichiometric compositions showed V_3Ga to be the major phase present. For hypostoichiometric compositions, V_6Ga_5 lines were identified in the X-ray patterns; while at hyperstoichiometric compositions, V lines were present.

The lattice parameter of V_3Ga also remained constant at 4.8165 ± 0.0015

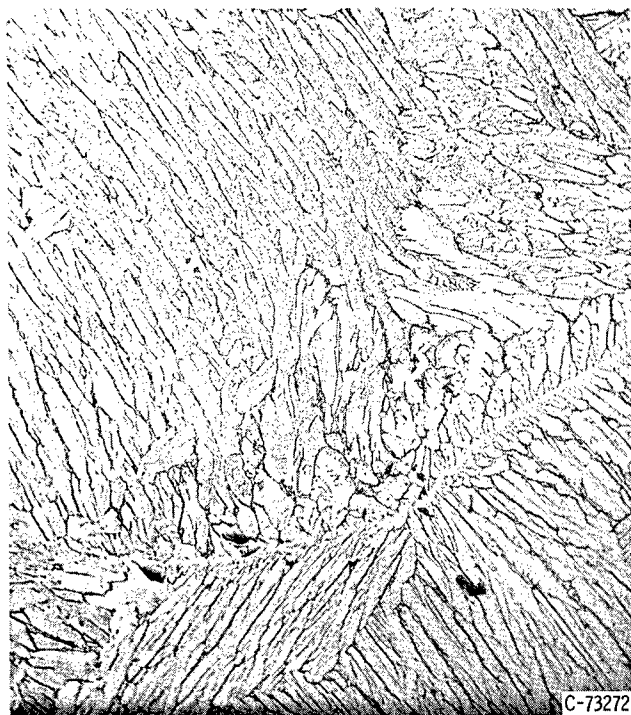


Figure 4. - Microstructure of sample containing 76.2 atomic percent vanadium. Primary phase, V_3Ga (white); secondary phase, V-Ga solution. Etchant, $4H_2O-3HNO_3-1HF$; X250.



Figure 5. - Electron micrograph of sample containing 74.8 atomic percent vanadium. Primary phase, V_3Ga matrix; second phase, V_6Ga_5 . X14,000.

angstroms for both hypostoichiometric and hyperstoichiometric compositions. This is in agreement with the value given in reference 8 of 4.816 ± 0.002 angstroms. The constancy of the lattice parameter observed here, the identification of second phases as equilibrium phases (either V_6Ga_5 or V), and the characteristic microstructures of near-stoichiometric compositions all suggest that single-phase V_3Ga exists over a very limited compositional range. Microhardness measurements of the light matrix phase of figures 3 and 4 (V_3Ga) gave a value of 920 DPH.

$V_3Ga + V$

A sample containing 85.6 atomic percent V was examined metallographically and by X-ray diffraction and found to be a single-phase V solid solution. The lattice parameter of this solid solution is 3.038 angstroms compared to 3.028 angstroms for pure V (ref. 9). This is not in agreement with reference 5, which reports a lattice parameter of 3.037 angstroms for a 94.85 atomic percent V solid solution.

The sample containing 77.0 atomic percent V definitely contained V_3Ga in addition to the V solid solution and gave a V lattice parameter of 3.043 angstroms. A useful lattice constant of V could not be obtained from the sample containing 76.2 atomic percent V because of the low intensities of V lines and some overlap with the V_3Ga lines.

Superconductivity Measurements

The sample containing 52.7 atomic percent V (primarily V_6Ga_5) was tested for superconductivity at 4.2° K and found to be normal. Reference 4 reported V_6Ga_5 to be normal to 2.1° K.

The sample containing 85.6 atomic percent V was also tested and found to be normal at 4.2° K. This result indicates that the critical temperature T_c of V is lowered more than 1° K by the addition of 14.3 atomic percent Ga in solution, based on a T_c of 5.3° K reported for pure V (ref. 10).

These results indicate that the phases in equilibrium with V_3Ga are normal at 4.2° K. Therefore, for near-stoichiometric compositions at 4.2° K, the microstructure consists of superconducting V_3Ga containing particles of nonsuperconducting second phase. These particles are generally of a continuous nature as opposed to isolated particles (figs. 3 to 5), and as such govern the size of the superconducting V_3Ga paths. Structures with the V_3Ga continuous path of the order of 2000 to 5000 angstroms wide have been observed in connection with this study. Critical field enhancement by decreasing the dimensions of the superconducting phase has been obtained in aluminum-lead composites (ref. 11) and a niobium-thorium eutectic alloy (ref. 12). In the case of V_3Ga , control of this dimension by heat treatment and/or compositional variations might offer a means of maximizing critical fields.

SUMMARY OF RESULTS

The vanadium-gallium (V-Ga) system within the compositional range from 50 to 100 atomic weight percent V was investigated. Samples prepared by melting were studied by X-ray diffraction and metallographic techniques after slow cooling from 1100° C. The following are the major results of this investigation.

1. The V_3Ga phase exists over a very limited compositional range near the stoichiometric composition.
2. The phases in equilibrium with V_3Ga at room temperature are V_6Ga_5 for hypostoichiometric compositions and V with Ga in solid solution for hyperstoichiometric compositions.
3. Both V_6Ga_5 and a V solid solution containing 14.3 atomic percent Ga are normal at 4.2° K.
4. The microstructural appearance of slightly hypostoichiometric and hyperstoichiometric compositions are essentially identical, with a second phase, either V_6Ga_5 or Ga saturated V, present as precipitate particles in the V_3Ga matrix.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 13, 1964.

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